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(54) Ink jet receptive recording media

(57) Ink jet ink receptive recording media are provided that contain a substrate having an ink receptive coating thereon. The coatings used to prepare the media contain a cellulose ether and an aluminum oxide particulate. Preferably, the coating compositions contain about 50% to about 95% of the cellulose ether on a weight/weight basis, based on the amount of solids in the coating composition, and preferably the cellulose ether has a hydroxyalkyl content of 0% to about 32% and a methoxy content of about 16% to about 32%. The aluminum oxide particulate utilized preferably possesses an average dispersed particle size of about 10 nanometers to about 200 nanometers, (more preferably of about 30 nanometers to about 170 nanometers), a pH that falls within the acidic to neutral pH range (more preferably from about pH 3 (acidic) up to about pH 7 (neutral)). The provided ink jet ink receptive recording media possess the combined properties of (i) a low level of ink cracking, (ii) good optical density, and (iii) a good dry time, when printed in an ink jet printing process.

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Description

[0001] This application is a continuation-in-part of copending U.S. Application Serial No. 08/730,309 filed October 11, 1996.

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Field of the Invention

[0002] The invention pertains to an ink jet ink receptive recording medium prepared by applying an ink jet receptive coating composition to a surface of a suitable base substrate.

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Background of the Invention

[0003] Ink jet ink receptive coating layers used in the preparation of ink jet ink receptive recording media have to meet a number of performance requirements. These requirements include dry time, color density, resolution, tack, color fidelity and lightfastness, as well as cost. There are many materials, both organic and inorganic, that have been proposed for this application. Among them, cellulose derivatives and alumina particulates have shown promising performance, and cellulose derivatives have been used alone or in combination with an inorganic pigment other than alumina. For example, U.S. Patent 4, 555,437 describes a hydroxyethyl cellulose coating, and U.S. Patent 4,575,465 describes a hydroxypropyl cellulose coating.

[0004] Alumina has been used as a filler or pigment for ink jet recording media. For example, U.S. Patent 4,780,356 discloses a two-layer coating that contains silica or alumina with a particle size of 0.1 µm - 50 µm, U.S. Patent 5,104,730 discloses a coating that contains pseudo-boehmite and polyvinyl alcohol, U.S. Patent 5,264,275 discusses a two-layer coating that contains pseudo-boehmite and polyvinyl alcohol/polyvinyl pyrrolidone.

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Summary of the Invention

[0005] The present invention provides an ink jet ink receptive coating composition that can be used in preparing ink jet recording media, which, upon printing, possess the improved combination of properties of (i) good black ink optical density, (ii) low pigment ink cracking, and (iii) good dry time.

[0006] The present invention also provides for an inventive ink jet ink receptive recording media, which is prepared by applying one of the instant inventive ink jet ink receptive coating compositions to a surface of a suitable base substrate.

[0007] Specifically, we provide an ink jet ink receptive coating composition that is useful in preparing ink jet recording media, wherein the coating composition - when appropriately applied to a suitable base substrate and subsequently printed upon in an ink jet printing process - provides ink jet recording media that offer the improved properties mentioned above.

[0008] Preferably, the inventive ink jet ink receptive coating composition that is useful in preparing inventive ink jet recording media comprises a cellulose ether in combination with an aluminum oxide particulate.

[0009] When a cellulose ether is used in the inventive coating compositions, it is preferably methylcellulose or a hydroxyalkyl methylcellulose. It is also preferable that the cellulose ether used in the inventive coating compositions possesses a hydroxyalkyl content of 0% to about 32% and a methoxy content of about 16% to about 32%, when tested according to ASTM D-3876 and ASTM D-2363. Furthermore, it is preferable for the cellulose ether to be present in the inventive coating compositions at a level of from about 50% to about 95% on a weight/weight basis, based on the amount of solids in the coating composition.

[0010] When an aluminum oxide particulate is used in the inventive coating composition, it preferably should possess the chemical formula Al_2O_3 . It should also preferably possess an average dispersed particle size of about 10 nm to about 200 nm, more preferably about 30 nm to about 170 nm. Further, an aluminum oxide particulate falling within the acidic to neutral pH range is preferred, with one falling in the pH range of from about pH 3 (acidic) to about pH 7 (neutral) being most preferred.

[0011] The good ink jet printing performance that is associated with the ink jet recording medium of the present invention, results from the fact that they comprise a suitable substrate having on a surface thereof an ink jet recording layer that is made from one of the inventive ink jet ink receptive coating compositions.

Detailed Description of the Invention

[0012] The following detailed description is provided as an aid to those desiring to practice the present invention. It is not to be construed as being unduly limiting to the present inventive discovery, since those of ordinary skill in the art will readily recognize that the embodiments of the inventors' discovery disclosed herein may be modified using standard techniques and materials known in the art, without departing from the spirit or scope of the present inventive discovery.

[0013]. In arriving at the present invention, the present inventors discovered that several design parameters are important to achieving the present invention. These design parameters include:

- 5 (1) Inorganic oxides, and preferably aluminum oxide, should be used in ink jet ink receptive coating compositions in combination with polymeric binders to achieve optimal performance.
- (2) Polyvinyl alcohol and polyvinyl pyrrolidone are not typically appropriate for use as binders for some ink jet recording media applications to achieve optimal performance.
- 10 (3) The use-of cellulose derivatives alone (*i.e.*, by themselves) in preparing ink jet ink receptive coating compositions does not result in an ink jet recording medium having the desired combination of properties to achieve optimal performance.
- (4) Not all cellulose derivatives are capable of providing an optimal performance in the desired properties in an ink jet recording medium, when present in the ink jet recording layer thereof.
- 15 (5) Many alumina pigments are unsuitable for use as an inorganic pigment in the present invention because of inappropriate characteristics that are associated therewith, such as size, reactivity, or a pH falling in the basic range (*i.e.*, > pH 7.0).

[0014] Accordingly, in order to achieve optimal performance, the inventive ink jet ink receptive recording media are prepared with ink jet coating compositions containing at least (i) a cellulose ether and (ii) an aluminum oxide particulate. Such ink jet ink receptive coating compositions of this invention preferably contain about 50% to about 95% of the cellulose ether therein, on a weight/weight basis, based on the amount of solids in the coating compositions.

[0015] The typical examples of cellulose ethers that are useful in the present invention are methylcellulose and hydroxyalkyl methylcelluloses, such as hydroxyethyl methylcellulose, hydroxypropyl methylcellulose and hydroxybutyl methylcellulose. Preferably, the cellulose ether should have a hydroxyalkyl content of 0% to about 32% and a methoxyl content of about 16% to about 32%.

[0016] The present inventors, in order to achieve optimal performance, utilize a form of aluminum oxide particulate that is stable, has a small particle size in order to prevent haze, and, preferably, has an acidic to neutral pH value in order to prevent dark fade of the printed ink jet recording product. Specifically, the present inventors have discovered that aluminum oxide particulates having the chemical formula Al_2O_3 and an average dispersed particle size of about 10 nanometers to about 200 nanometers are preferred and such particulates have an average dispersed particle size of about 30 nanometers to about 170 nanometers are most preferred. Also, the pH of the present inventors' aluminum oxide particulates falls within the acidic to neutral pH range, and is more preferably from about pH 3 (acidic) up to about pH 7 (neutral).

[0017] According to a preferred embodiment of the invention, the ink jet ink receptive coating compositions comprise about 0.01 to about 15% by weight of particulates therein (not including the aforementioned alumina particulates), based on the weight of the dry coating. In this way it is possible to modify the surface properties of the ink jet recording layer in the prepared ink jet recording media. Examples of such particulates include inorganic particulates, such as silica, kaolin, glass beads, calcium carbonate, titanium oxide, barium sulfate, aluminum silicate, zirconium oxide and tin oxide and organic particulate such as polyolefins, polystyrene, polyurethane, starch, poly(methyl methacrylate) and polytetrafluoroethylene.

[0018] In practice, various additives may also be employed in the ink jet ink receptive coating compositions of this invention. These additives can include surface active agents which control the wetting or spreading action of coating solutions, antistatic agents, suspending agents and acidic compounds to control pH of the coating. Other additives may also be used, if so desired.

[0019] The ink jet ink receptive coating compositions of this invention can be applied to a surface of a variety of different base substrates (*e.g.*, transparent plastics, translucent plastics, matte plastics, opaque plastics or papers), to prepare one of the inventive ink jet recording media. Suitable polymeric materials for use as the base substrate include polyester, cellulose, esters, polystyrene, polypropylene, poly(vinyl acetate), polycarbonate, and the like. Poly(ethylene terephthalate) film is a particularly preferred base substrate. Further, while almost any paper can be used as the base substrate, clay coated or polyolefin coated papers are particularly preferred as base substrate papers. The thickness of the base substrate is not particularly restricted but should generally be in the range of from about 1 to about 10 mils, preferably from about 3.0 to about 5.0 mils. The base substrate may be pretreated to enhance adhesion of the ink receptive coating thereto.

[0020] The thickness of the inventive coating is not particularly restricted, but should generally be in the range from about 2 grams per square meter to about 30 grams per square meter, on a surface of the base substrate.

[0021] A surface of the base substrate that does not bear the ink jet ink receptive coating may have a backing material placed thereon in order to reduce electrostatic charge and to reduce sheet-to-sheet friction and sticking and reduce curl, if so desired. The backing material may either be a polymeric coating, a polymer film or paper.

[0022] Any number of coating methods may be employed to coat the ink jet ink receptive coating composition onto

the surface of the base substrate. For example, roller coating, blade coating, wire-bar coating, dip coating, extrusion coating, air knife coating, curtain coating, slide coating, doctor coating or gravure coating, may be used and are well known in the art.

5 [0023] The following Examples are given merely as illustrative of the invention and are not to be considered as limiting thereto. In the Examples "parts" refers to parts by weight, based on the total weight of solids in the coating compositions.

EXAMPLE I

10 [0024] A coating composition is prepared according to the following formulation:

Ink Receptive Coating Composition:

[0025]

15

Methylcellulose ¹	3.2 parts
Hydroxypropyl methylcellulose ²	6.1 parts
Alumina Sol ³	5.4 parts
Water	85.3 parts
Crosslinked poly(methyl methacrylate) ⁴	0.01 parts

25

1. Methocel A15LV, Dow Chemical Company
2. Methocel K3LV, Dow Chemical Company
3. Dispal 23N4-20, Vista Chemical Company
4. Soken Chemical & Engineering Company, Ltd.

30

[0026] The coating is applied to a polyester film (ICI Films) using a No. 24 Meyer rod, and the coating is dried at about 130°C for about 2 minutes.

EXAMPLE II

35

[0027] A coating composition is prepared according to the following formulation:

Ink Receptive Coating Composition:

[0028]

Hydroxypropyl methylcellulose ¹	4.1 parts
Alumina Sol ²	3.8 parts
Water	92.1 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

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1. Methocel K35LV, Dow Chemical Company
2. Dispal 11N7-12, Vista Chemical Company

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55 [0029] The coating is applied to a polyester film (ICI Films) using a No. 50 Meyer rod, and is dried at about 130°C for about 2 minutes.

EXAMPLE III

[0030] A coating composition is prepared according to the following formulation:

5 Ink Receptive Coating Composition:

[0031]

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15	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">Hydroxypropyl methylcellulose¹</td><td style="padding: 2px;">2.6 parts</td></tr> <tr> <td style="padding: 2px;">Alumina Sol²</td><td style="padding: 2px;">2.4 parts</td></tr> <tr> <td style="padding: 2px;">Water</td><td style="padding: 2px;">95.0 parts</td></tr> <tr> <td style="padding: 2px;">Crosslinked poly (methyl methacrylate)</td><td style="padding: 2px;">0.01 parts</td></tr> </table>	Hydroxypropyl methylcellulose ¹	2.6 parts	Alumina Sol ²	2.4 parts	Water	95.0 parts	Crosslinked poly (methyl methacrylate)	0.01 parts
Hydroxypropyl methylcellulose ¹	2.6 parts								
Alumina Sol ²	2.4 parts								
Water	95.0 parts								
Crosslinked poly (methyl methacrylate)	0.01 parts								

1. Methocel K100LV, Dow Chemical Company
 2. Nyacol AL20, Nyacol Products, Inc.

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[0032] The coating is applied to a polyester film (ICI Films) using a No. 70 Meyer rod, and is dried at about 130°C for about 2 minutes.

EXAMPLE IV

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[0033] A coating composition is prepared according to the following formulation:

Ink Receptive Coating Composition:

30 [0034]

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40	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">Methylcellulose¹</td><td style="padding: 2px;">8 parts</td></tr> <tr> <td style="padding: 2px;">Alumina Sol²</td><td style="padding: 2px;">6 parts</td></tr> <tr> <td style="padding: 2px;">Water</td><td style="padding: 2px;">86 parts</td></tr> </table>	Methylcellulose ¹	8 parts	Alumina Sol ²	6 parts	Water	86 parts
Methylcellulose ¹	8 parts						
Alumina Sol ²	6 parts						
Water	86 parts						

1. Methocel A15LV, Dow Chemical Company
 2. Dispal 23N4-20, Vista Chemical Company

45

[0035] The coating is applied to a polyester film (ICI Films) using a No. 50 Meyer rod, and the coating is dried at about 130°C for about 2 minutes.

COMPARATIVE EXAMPLE C-I

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[0036] A coating composition is prepared according to the following formulation:

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Ink Receptive Coating Composition:

[0037]

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Methylcellulose sodium salt ¹	4.1 parts
Alumina Sol ²	3.7 parts
Water	92.2 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

1. Hercules Inc.
2. Dispal 23N4-20, Vista Chemical Company

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[0038] The coating is applied to a polyester film (ICI Films) using a No. 50 Meyer rod, and is dried at about 130°C for about 2 minutes.

20 COMPARATIVE EXAMPLE C-II

[0039] A coating composition is prepared according to the following formulation:

Ink Receptive Coating Composition:

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[0040]

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Polyvinyl alcohol ¹	5.8 parts
Alumina Sol ²	5.3 parts
Water	88.9 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

1. Airvol 823, Air Products and Chemicals, Inc.
2. Dispal 23N4-20, Vista Chemical Company

40 [0041] The coating is applied to a polyester film (ICI Films) using a No. 50 Meyer rod, and is dried at about 130°C for about 2 minutes.

COMPARATIVE EXAMPLE C-III

45 [0042] A coating composition is prepared according to the following formulation:

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Ink Receptive Coating Composition:

[0043]

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Polyvinyl pyrrolidone ¹	5.7 parts
Alumina Sol ²	5.2 parts
Water	89.1 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

1. PVP K-90, ISP Technologies, Inc.
 2. Dispal 11N7-12, Vista Chemical Company

15

[0044] The coating is applied to a polyester film (ICI Films) using a No. 50 Meyer rod, and is dried at about 130°C for about 2 minutes.

20 COMPARATIVE EXAMPLE C-IV

[0045] A coating composition is prepared according to the following formulation:

Ink Receptive Coating Composition:

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[0046]

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Hydroxypropyl methylcellulose ¹	15 parts
Water	85 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

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1. Methocel K3LV, Dow Chemical Company

[0047] The coating is applied to a polyester film (ICI Films) using a No. 24 Meyer rod, and is dried at about 130°C for about 2 minutes.

40 COMPARATIVE EXAMPLE C-V

[0048] A coating composition is prepared according to the following formulation:

45

Ink Receptive Coating Composition:

[0049]

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Hydroxypropyl methylcellulose ¹	9.7 parts
Colloidal Silica Sol ²	8.8 parts
Water	81.5 parts
Crosslinked poly(methyl methacrylate)	0.01 parts

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1. Methocel K3LV, Dow Chemical Company
 2. Ludox SK, Dupont Company

[0050] The coating is applied to a polyester film (ICI Films) using a No. 24 Meyer rod, and is dried at about 130°C for about 2 minutes.

[0051] Each of the prepared ink jet recording media of Examples I-III and Comparative Examples C-I to C-V, are evaluated to determine whether they offer the following improved combination of properties of (i) a good level of black ink optical density, (ii) a low level of pigment ink cracking, and (iii) a good dry time, when printed in an ink jet printing process.

[0052] The prepared ink jet recording media are evaluated by printing on the ink jet recording surface thereof a test plot with a Hewlett Packard DESKJET 660C printer using HP 51629A and HP 51649A ink cartridges. The black ink is pigment based in the evaluation.

[0053] The black ink optical density of each test sample is measured with a MACBETH TD 904 densitometer (Macbeth Process Measurements) using the beige filter setting. A measurement is taken at three different locations along a solid black image stripe. The average of the three measurements is the black ink optical density.

[0054] The amount of pigmented ink cracking that is associated with each sample is quantitatively rated with a numerical scale of 0 to 5 (0=worst and 5=best). Each Example and Comparative Example is imaged with a test print. The Examples are given a numerical rating by comparing the Examples to standard prints that exhibit each level of ink cracking.

[0055] The dry time of each Example is measured by first printing each example with the test plot. The Example is then placed on top of a 20 lb. ream of XEROX 4200 paper. This is time zero (t_0). Thereafter, at thirty second intervals, a sheet of white bond paper is placed onto the surface of the Example, and then another 20 lb. ream of XEROX 4200 paper is placed on top of the white bond paper. After five seconds, the top ream of paper and white bond paper is removed from on top of the Example. The Example is dry when no transfer of ink between the print and the white bond paper occurs, which is termed the dry time (t_{dry}).

[0056] The black ink optical density, ink cracking and dry time (measured in minutes) for each Example and Comparative Example is provided in Table I.

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TABLE I

PERFORMANCE EVALUATION OF THE COATINGS			
Example	Black Ink Optical Density	Ink Cracking	Dry Time
I	2.09	4	2.5
II	2.07	4	2
III	2.11	4	2
IV	2.08	5	25
C-I	1.19	1	>5
C-II	1.37	1	3.5
C-III	1.21	1	4.5
C-IV	1.08	1	3.5
C-V	.93	0	3.5

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[0057] As shown in Table I, Examples I to III all exhibited improved black ink optical density, a low level of pigment ink cracking, and a good dry time as compared to the Comparative Examples C-I to C-V.

[0058] The pigmented black ink optical density is inversely proportional to ink cracking, with pigment ink cracking decreasing the black ink optical density. When ink cracking is rated below 3, ink cracking is clearly visible to the eye, and the ink jet recording media are not suitable for many commercial applications.

[0059] The improved dry time of the examples allows a higher through put of the media in ink jet printing devices.

[0060] Each of the patents and publications referred to herein are incorporated by reference in their entirety into the present application.

55 Claims

1. An ink jet recording medium that comprises: a base substrate having coated on a surface thereof an ink jet ink receptive layer that contains a cellulose ether and an aluminum oxide particulate.

2. The ink jet recording medium according to claim 1, wherein said cellulose ether is methylcellulose or a hydroxyalkyl methylcellulose.
3. The ink jet recording medium according to claim 1 or 2, wherein said cellulose ether has a hydroxyalkyl content of 5% to about 32% and a methoxy content of about 16% to about 32%.
4. The ink jet recording medium according to any of claims 1-3, wherein said ink jet recording layer contains about 10% to about 95% of said cellulose ether on a weight/weight basis, based on the amount of solids in said coating layer.
5. The ink jet recording medium according to any of claims 1-4, wherein said aluminum oxide particulate has the chemical formula Al₂O₃.
6. The ink jet recording medium according to any of claims 1-5, wherein said aluminum oxide particulate has an average dispersed particle size of from about 10 nm to about 200 nm.
7. The ink jet recording medium according to claim 6, wherein said aluminum oxide particulate has an average dispersed particle size of from about 30 nm to about 170 nm.
8. The ink jet recording medium according to any of claims 1-6, wherein said aluminum oxide particulate has a pH in the acidic to neutral range.
9. The ink jet recording medium according to claim 8, wherein said aluminum oxide particulate has a pH in the range of about pH 3 to about pH 7.
- 25 10. The ink jet recording medium according to any of claims 2-9, wherein said cellulose ether is selected from the group consisting of methylcellulose, hydroxyethyl methylcellulose, hydroxypropyl methylcellulose and hydroxybutyl methylcellulose.
- 30 11. The ink jet recording medium according to any of claims 1-10, wherein said ink jet recording layer additionally comprises an inorganic particulate that is selected from the group consisting of silica, kaolin, glass beads, calcium carbonate, titanium oxide, barium sulfate, aluminum silicate, zirconium oxide and tin oxide.
- 35 12. The ink jet recording medium according to any of claims 1-11, wherein said ink jet recording layer additionally comprises an organic particulate that is selected from the group consisting of polyolefin, polystyrene, polyurethane, starch, poly(methyl methacrylate) and polytetrafluoroethylene.
- 40 13. The ink jet recording medium according to any of claims 1-12, wherein the base substrate is selected from the group consisting of a transparent plastic substrate, an opaque plastic substrate, a matte plastic substrate, a translucent substrate and a paper.

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EUROPEAN SEARCH REPORT

Application Number

EP 99 11 3728

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	EP 0 835 762 A (ARKWRIGHT INC) 15 April 1998 (1998-04-15) * the whole document *	1-13	B41M5/00
X	PATENT ABSTRACTS OF JAPAN vol. 199, no. 706, 30 June 1997 (1997-06-30) & JP 09 048173 A (NICHIBAN CO LTD), 18 February 1997 (1997-02-18) * abstract *	1-13	
X	WO 97 22467 A (PPG INDUSTRIES INC) 26 June 1997 (1997-06-26) * page 1, line 8 - line 22 * * page 19, line 3 - page 22, line 16 * * claims 1,4-6,15,16,19-21 *	1-13	
X	WO 88 06532 A (AM INT) 7 September 1988 (1988-09-07) * page 3, line 5 - line 20 * * page 4, line 22 - page 5, line 8 * * page 5, line 22 - page 11, line 3 *	1-13	TECHNICAL FIELDS SEARCHED (Int.Cl.) B41M
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	25 October 1999	Markham, R	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 11 3728

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-10-1999

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0835762	A	15-04-1998		CA 2217525 A JP 10119429 A		11-04-1998 12-05-1998
JP 09048173	A	18-02-1997		NONE		
WO 9722467	A	26-06-1997		AU 704721 B AU 1279697 A CA 2239056 A CN 1208374 A		29-04-1999 14-07-1997 26-06-1997 17-02-1999
WO 8806532	A	07-09-1988		AU 615183 B AU 1425488 A DE 3882621 A DE 3882621 T EP 0305478 A JP 1502805 T US 5198306 A		26-09-1991 26-09-1988 02-09-1993 04-11-1993 08-03-1989 28-09-1989 30-03-1993